

ON THE ABSORPTION AND EMISSION SPECTRA OF RARE EARTH CRYSTALS

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Plate XI

ABSTRACT. In this paper the results of investigation of the emission and absorption spectra of the rare earth ions like La^{+++} , Ce^{+++} , etc., in crystals are given. An attempt has been made to correlate their absorption and emission spectra with special reference to Ce^{+++} ions.

It has been observed that the La^{+++} ions in crystals do not fluoresce. The emission spectra due to Ce^{+++} ions in the chloride and the sulphate crystals consist of two discrete bands. The positions of the bands are slightly different in the two salts but they occupy almost the same positions whether the salts investigated are hydrated or dehydrated. The spectra due to CeF_3 consist of three such emission bands; further on excitation with high frequency a weak luminescence appears on the long wave-side of the bands.

The strong and discrete emission bands have been supposed to be due to the true fluorescence of the Ce^{+++} ions. In conformity with the explanation of the absorption spectra due to Ce^{+++} ions by Bose and the writer, the origin of these emission bands has been ascribed to the transitions $5D \rightarrow 4F$ in Ce^{+++} ions. The two bands in the chloride and the sulphate and the two lower frequency bands in the fluoride arise from the transitions $5^2D_{5/2} \rightarrow 4^2F_{5/2, 7/2}$, while the third band in CeF_3 is due to $5^2D_{3/2} \rightarrow 4^2F_{5/2}$. It has been shown that there is a correlation between the frequency of the emission bands and the corresponding absorption frequencies. The absence of the third band in the other two crystals has been discussed.

The origin of the weak luminescence is not clearly understood. It has been suggested that it is due to an excitation of the F^+ ion by a collision of the second kind, with the excited Ce^{+++} ions, the process resembling somewhat a case of sensitized fluorescence.

INTRODUCTION

In a previous paper* the fluorescence spectra of a few rare earth ions, viz., La^{+++} , Ce^{+++} , Pr^{+++} and Nd^{+++} in solution were investigated by the writer.

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It was observed that in solution all the ions give rise to a common diffuse band in emission, while in Pr^{+++} and Nd^{+++} ions there are respectively two and three additional diffuse bands. For the emission of the common fluorescence band by the four rare earth ions in solution, the following mechanism was proposed. The emission centres were assumed to be the metal complex $(\text{Me}^{+++} \cdot n\text{H}_2\text{O})$, in which the H_2O groups are polarised in the field of the Me^{+++} ion. Even in the case of $(\text{La}^{+++} \cdot n\text{H}_2\text{O})$, which has no electron in the $4f$ shell, the solution shows finite continuous absorption in the ultra-violet; the absorption of radiation is supposed to be by the complex as a whole leading to an excitation of the polarised H_2O group and re-emitted as fluorescence radiation. This fluorescence is similar in mechanism to that shown by uranyl groups $[\text{U}(\text{O}_2)]^{++}$. The fluorescence radiation emitted by the solutions containing Ce^{+++} , Pr^{+++} and Nd^{+++} are much stronger than that by the La solution. This can be interpreted in the following way. In the case of $(\text{Ce}^{+++} \cdot n\text{H}_2\text{O})$, for example, besides the continuous absorption by the complex as a whole there are discontinuous absorption bands due to the absorption by the Ce^{+++} ions ($4f \rightarrow 5D$). The corresponding ion is in a metastable excited state, and before it comes back to its ground state by the emission of radiation, it can transfer its energy by collision with other hydrated ions. These latter become excited and emit energy by re-emission, with a frequency equal to that given by the lanthanum complex. If ν_0 represents the frequency associated with this transition, the presence of the additional bands was explained as having frequencies $(\nu_0 \pm \nu_1)$ where ν_1 represents one or other of the characteristic frequencies of the Me^{+++} ion.

Later on, the fluorescence spectra of the same ions were investigated using crystals having different anions, both in the hydrated and in the anhydrous state. It was noticed that the width of the emission bands was much reduced; further the spectra of the different crystals having the same cations were found to be different. But no perceptible change could be found between the emission spectra of the same crystal when hydrated or in the dehydrated state. The purpose of the present paper is to study the correlations between the emission and absorption spectra of these ions in crystals and to attempt an explanation of the origin of the emission spectra in crystals with special reference to Ce^{+++} ion. But before we proceed to discuss the absorption and emission spectra of Ce^{+++} etc. ions, let us give a brief résumé of the previous knowledge of the fluorescence spectra of the rare earth crystals.

PREVIOUS KNOWLEDGE OF THE FLUORESCENCE SPECTRA OF THE RARE EARTHS

The true fluorescence of the rare earth ions was first observed by Tomaschek and Deutschbein¹ in pure hydrated crystals of Sm, Eu, Tb and Dy. The spectra

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consist of groups of more or less sharp and diffuse lines in the visible region, which increased in sharpness on lowering the temperature of the crystals. Later on, Gobrecht² extended the investigations to the infra-red side and by considering the complete set of emission data was able to obtain some correlation between the emission and the absorption spectra of the respective ions.

In the rare earth ions the different combinations of the l - and s -vectors of the $4f$ electrons according to the Russell-Saunders coupling give rise to a number of $4f$ -levels. Of these the term having the smallest inner quantum number consistent with the highest multiplicity and l -moment represents the ground state for the members in the first half of the series; for the latter half which have inverted terms the ground term will have the corresponding highest j -value. In the process of absorption the $4f$ -electrons are excited from the ground state to the upper states allowed by the selection principle. In the crystals on account of the strong crystalline electric field the quadrupole radiation is also possible so that the selection rules will be due to both the dipole and the quadrupole radiation. Further in the strong inhomogeneous electric field each of the said $4f$ -levels is perturbed and their degeneracy is partly removed; so instead of a single line a group of lines arises out of each of those transitions.

In emission,* on the other hand, the final state will be generally the ground state or some other state in its neighbourhood while the initial state may be the upper ones allowed by the selection rules. It is generally found that the transitions ending in the ground state give rise to the strong components in the emission spectra. Gobrecht has shown that for the four ions investigated there is an agreement between the number of strong emission groups and the multiplicity of the ground term. This is shown in table I. He also showed that the over-all splitting of the ground term obtained from the emission spectra leads to a correct value of the screening constant for the four ions investigated. Tomaschek and Melnert³ recently observed the sharp fluorescence spectra in Gd^{+++} ions using hydrated sulphate crystals. It consists of one group of principal emission lines in the ultra-violet, which coincides in position with the group of absorption lines of lowest frequency due to the same ion. In Gd^{+++} ion having an 8S -term for its ground state only one group of emission lines is to be anticipated. It is thus clear that the fluorescence spectra observed in these five ions are explicable on the usual theory of emission spectra of such ions. But it is not understood, so far, why the sharp emission spectra are observed only in these five rare earth ions, while the absorption spectra of a similar nature are known to be present in all the members of the series excepting only Ce^{+++} and Yb^{+++} .

* The mechanism of emission will be discussed more fully later on in the paper.

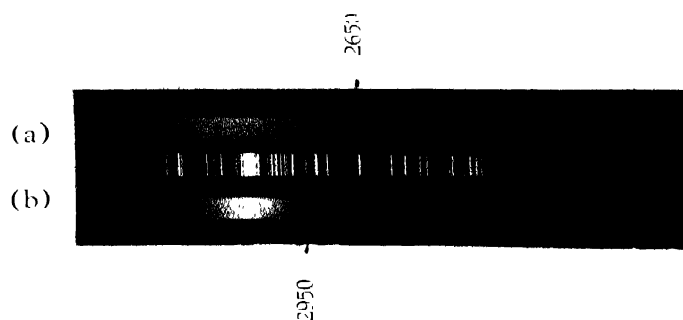
TABLE I

(Fluorescence spectra due to different rare earth ions in hydrated crystals)

Ion.	Ground State	Emission group.	Average intensity	Average position.	Final level.
Sm ⁺⁺⁺	⁶ H	1	5	9,755 cm. ⁻¹	⁶ F _{7/2}
		2	5	10,773 "	⁶ F _{5/2}
		3	7	11,295 "	⁶ H _{1/2} ⁶
		4	7	12,844 "	⁶ H _{1/2} ⁸
		5	7	14,189 "	⁶ H _{1/2} ¹
		6	6	15,574 "	⁶ H _{3/2}
		7	6	16,710 "	⁶ H _{7/2}
		8	4	17,800 "	⁶ H _{5/2}
Eu ⁺⁺⁺	⁷ F	1	9	12,215 cm. ⁻¹	⁷ F ₆
		2	4	13,330 "	⁷ F ₆
		3	5	14,340 "	⁷ F ₄
		4	5	15,325 "	⁷ F ₃
		5	9	16,240 "	⁷ F ₂
		6	8	16,877 "	⁷ F ₁
		7	3	17,108 "	⁷ F ₀
		*8	3	17,968 "	
		*9	3	18,711 "	
		*10	3	19,049 "	
Tb ⁺⁺⁺	⁷ F	1	8	14,734 cm. ⁻¹	⁷ F ₀
		2	7	14,938 "	⁷ F ₁
		3	5	15,399 "	⁷ F ₂
		4	6	16,145 "	⁷ F ₃
		5	6	17,076 "	⁷ F ₄
		6	9	18,334 "	⁷ F ₅
		7	5	20,483 "	⁷ F ₆
Dy ⁺⁺⁺	⁶ H	1	5	10,269 cm. ⁻¹	⁶ H _{5/2}
		2	6	11,732 "	⁶ H _{7/2}
		3	5	13,129 "	⁶ H _{3/2}
		*4	4	15,113 "	⁶ H _{1/2} ¹
		5	4	17,395 "	⁶ H _{1/2} ²
		6	5	20,699 "	⁶ H _{1/2} ⁶

* These groups are due to transitions from a level above the first excited state.

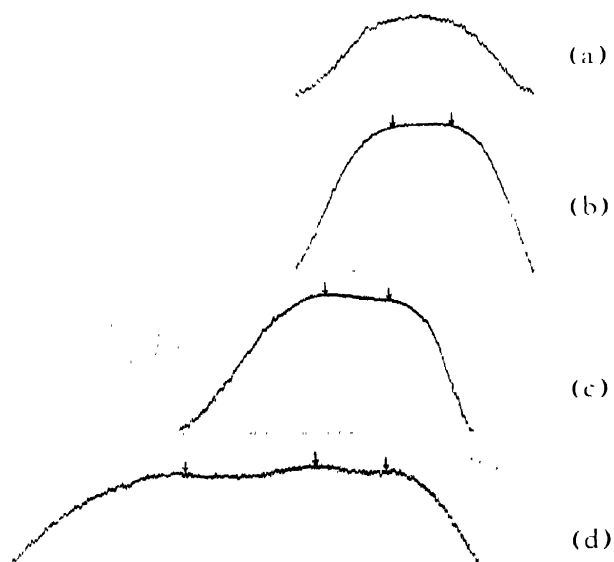
Figure 1.

Absorption spectra of CeF_3

(a) Using a very thin layer.

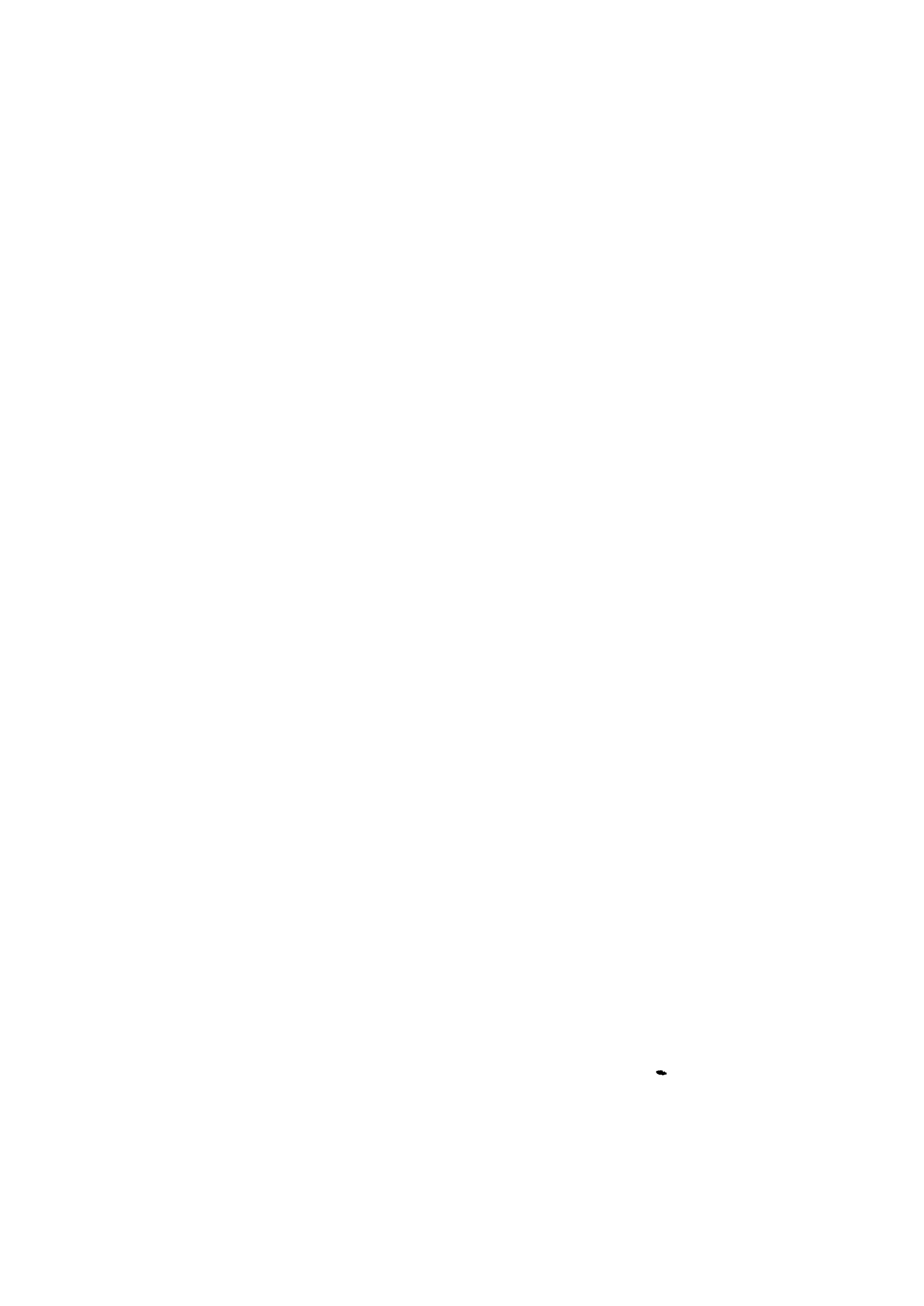
(b) Using a thicker layer.

Figure 2.



Microphotometric records of fluorescence spectra.

- (a) CeCl_3 soln.—one band with its centre at $28,220\text{cm}^{-1}$
 (b) CeCl_3 crystals—two bands at $26,838$; $29,631\text{cm}^{-1}$
 (c) $\text{Ce}_2(\text{SO}_4)_3$ crystals—two bands at $29,655$; $32,400\text{cm}^{-1}$
 (d) CeF_3 crystals—three bands at $29,655$; $32,450$; $36,095\text{cm}^{-1}$



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FLUORESCENCE SPECTRA OF THE RARE EARTH IONS INVESTIGATED

The fluorescence spectra of the first four ions of the rare earth series, *viz.*, La^{+++} , Ce^{+++} , Pr^{+++} and Nd^{+++} were investigated using hydrated and dehydrated crystals. The fluorescence was observed using monochromatic exciting radiations. A detailed account of the method of experimental investigation is given in a previous paper by the writer.⁴ It was found that La^{+++} ions in crystals do not fluoresce. In Ce^{+++} ions, on the other hand, interesting results were obtained; both the position and the number of the bands were found to vary with the different anions used. The results are given in table II. The investigations with Pr^{+++} and Nd^{+++} ion are now being repeated with extra pure samples but no evidence of any fluorescence has been obtained in the near ultra-violet.*

TABLE II

Fluorescence bands of Ce^{+++} ions in different hydrated and anhydrous crystals

Exciting radiation A.U.	Fluorescence radiation A.U.		
	Chloride (anhydrous).	Sulphate (hydrated and anhydrous).	Fluoride.
(a) 2750	3900-3200	1.3440-3305 2.3205-2990	1.3440-3305 2.3206-2970
(b) 2550	,,	1.3440-3305 2.3205-2990	1.3440-3305 2.3205-2970 3.2800-2740 4085-3440
(c) 2300	,	1.3440-3305 2.3205-2990	1.3440-3305 2.3200-2970 3.2800-2740 4085-3440
(d) 2100	,	1.3440-3305 2.3205-2990	1.3440-3305 2.3200-2970 3.2800-2740

* The investigation is now being carried on with Fluorite Spectrograph and Ilford's Q-plates.

La^{+++} ions in solution fluoresce but not when they form part of a crystal. The continuous absorption and the fluorescence emission in the solution is by the metallic complex $\text{La}^{+++} n\text{H}_2\text{O}$. In the crystal, on the other hand, the absorption of radiation is by the lattice as a whole, and this is dissipated in the form of lattice oscillation. In order to understand the origin of the emission spectra due to Ce^{+++} ions in the different crystals it seemed necessary to investigate the absorption spectra of the respective crystals.

ON THE ABSORPTION SPECTRA DUE TO Ce^{+++} IONS

The absorption spectra due to Ce^{+++} ions were observed by Bose and Datta⁵ in solution and by Freed⁷ using hydrated mixed crystals of Ce and La. It was found that the spectra consist of broad bands, which do not undergo any change with the lowering of temperature of the crystals. But the positions of the bands are altered slightly by changing the anions. These are shown in table III.

TABLE III

(Absorption spectra of Ce^{+++} ions in solution and in crystals)

Bands.	Position of the bands in A.U.		
	CeCl_3 soln. (1)	$\text{Ce}_2(\text{SO}_4)_3$ soln. (2)	$\text{La}(\text{Ce})\text{Cl}_6 \cdot 6\text{H}_2\text{O}$. (3)
I	2970	2960	3020
II	2525	2540	2775
III	2380	2400	2455
IV	2225	2230	2300

(1) By Bose and Datta.⁵

(2) By Roberts and Wallace.⁶

(3) By Freed.⁷

In course of the present work, the absorption spectra of CeF_3 crystals were investigated. As single crystals of CeF_3 could not be obtained, the investigation was carried on by the reflection method using extremely thin layer of the salt. In order to obtain a uniformly thin deposit, a small quantity of the salt was finely powdered and then shaken with distilled water in a beaker. After allowing some time for the heavier particles to settle down, a clean quartz plate was carefully introduced and kept suspended horizontally inside the water. After a

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long time when the fine particles settled down, the clear water was siphoned out and the quartz disc was dried up. In this way uniform deposits of varying thickness were prepared. The absorption spectra, obtained by using a hydrogen discharge tube, is shown in plate XI. It was found that using even the thinnest deposit the absorption was of a continuous nature and so no definite conclusion could be reached. But it was noticed that on diminishing the thickness of the deposit the long wavelength limit of the continuous absorption shifts from about 3100\AA° to 2600\AA° . It indicates the existence of a very weak band in the neighbourhood of 3000\AA° .

In a recent paper by Bose and the writer⁸ on the origin colour of paramagnetic ions in solution, the absorption spectra of Ce^{+++} ions in solution were explained to be due to the transition $4^2F_{5/2} \rightarrow 5^2D_{5/2, 3/2}$. In Ce^{+++}

ions $4f$ is the ground state and $5d$ is the first virtual state whose average position in the case of vapour was taken to be at $50,982 \text{ cm.}^{-1}$ as given by Lang.⁹ In solution the ground term $4F$ being screened by the $(5s, 1)$ octet shell remains unaffected, but the virtual $(5d)$ states are strongly perturbed by the influence of the neighbouring molecules.

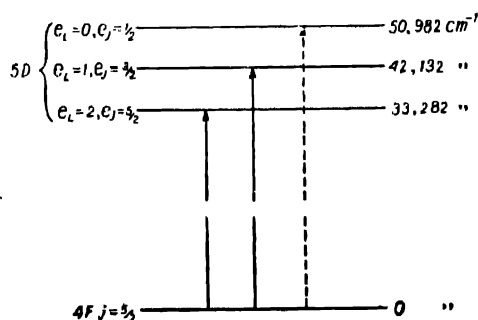


FIGURE 1

The scheme of energy levels proposed to explain the absorption spectra is shown in figure 1. The $5D$ level is pictured as split up into three sub-levels. The relative positions of the sub-levels were calculated from the formula given below,

$$\Delta v = Ne \cdot \Delta e_L \cdot K'$$

where Ne = ionic charge,

Δe_L = change in the electric quantum number,

K' = a constant for all ions having a particular state.

putting $Ne=3$, $e_L = 0, 1$ and 2 and $K' = 2950 \text{ cm.}^{-1}$

the average value of the constant for all ions having a D -state. In the process of absorption the $4F$ electron may occupy one or other of the three $5D$ levels and so three diffuse bands are expected as shown by the arrows. The agreement between the observed and the calculated positions is shown in table IV.

TABLE IV

Bands.	$\lambda(\text{A.}\mu.)$	$\nu(\text{Cm.}^{-1})$	C. G. (Cm. $^{-1}$)	$\nu(\text{Calcd.})$	Transitions.
I	2970	33,660	33,660	33,282 cm. $^{-1}$	$4F_{5/2} \rightarrow 5D_{5/2}$ ($e_L = 2$)
II	2525	39,592			
III	2380	42,004	42,175	42,132 ,,	$4F_{5/2} \rightarrow 5D_{3/2}$ ($e_L = 1$)
IV	2225	44,930	—	50,982 ,,	$4F_{5/2} \rightarrow 5D_{1/2}$ ($e_L = 0$)

In table III it is found that the absorption spectra due to Ce^{+++} ions in hydrated crystals are, more or less, similar to that found in solution. It may be supposed, therefore, that the splitting up of the $5D$ state in these hydrated crystals will be somewhat similar to that taking place in solution. So that a similar energy level diagram as shown in figure 1 will account for the absorption spectra of such crystals, only the value of the constant K' will be slightly modified by the different ions present.

ON THE EMISSION SPECTRA DUE TO Ce^{+++} IONS IN CRYSTALS

The results of investigation on the fluorescence spectra of Ce^{+++} ions in crystal are given in table III. It was found that in CeCl_3 crystals the emission band occupies the same position as in the corresponding aqueous solution. But from an examination of the microphotometric record of the spectrum it appeared to consist of two diffuse bands overlapping each other. In the sulphate crystals the two bands are more distinct and they occupy the same position whether obtained from the hydrated or the dehydrated crystals; but the position of the bands in either case is displaced slightly to the high frequency side as compared with that of $\text{Ce}_2(\text{SO}_4)_3$ solution. The total width of the two bands is same in either of the above cases and is nearly equal to that of the common fluorescence band observed in solution. In CeF_3 crystals three emission bands were noticed, of which the first two coincide in position with those due to the sulphate crystals. The third band on the higher frequency side appeared when the exciting frequency was high and along with this band a weak and diffuse luminescence appeared on

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the longer wavelength side of the principal emission bands. The microphotometric records of the emission spectra are shown in plate XI. The centres of gravity of the bands obtained in the different crystals using the highest frequency used, *viz.*, $48 \times 10^3 \text{ cm.}^{-1}$ nearly are given in table V.

TABLE V

Centres of gravity of the Fluorescence bands due to Ce^{+++} ions in crystals

Exciting frequency.	Fluorescence bands emitted		
	Chloride.	Sulphate	Fluoride.
$48 \times 10^3 \text{ cm.}^{-1}$	(1) 26,838 cm.^{-1} (2) 29,621 „	(1) 29,655 cm.^{-1} (2) 32,400 „	(1) 29,655 cm.^{-1} (2) 32,450 „ (3) 36,095 „

The origin of these emission spectra will now be discussed in the light of the present theories of luminescence of solids. In the case of crystals like those investigated here, there are the following alternative possibilities, when light of suitable frequency is incident on them, *viz.*,

(1) The ultra-violet light may be absorbed by the Ce^{+++} ions; (a) this may result in emission by the excited Ce^{+++} ions of the crystals. This gives rise to the true fluorescence; (b) there may be emission by transference of energy to the anion or a molecule attached to the Ce^{+++} ion by a collision of the second kind. This will be somewhat analogous to 'sensitized fluorescence.'

(2) Above a certain frequency the anion may begin to compete with the cation in absorption of radiation. At this stage no further emission levels of the cation may be excited by increasing the frequency of the exciting radiation.

ORIGIN OF THE FLUORESCENCE BANDS

In the different crystals containing Ce^{+++} ion the stronger emission bands observed are evidently due to the true fluorescence of the cation. Their origin is, therefore, due to the possibility 1 (a), where Ce^{+++} ions act as the absorbing and the emitting centres. In order to specify the different transitions in Ce^{+++} ions, which may give rise to the respective emission bands, we shall discuss in brief the mechanism of fluorescence of solids as it is pictured now-a-days.

In the interior of a solid, an electron shares the vibration energy of the lattice and so the energy levels instead of being very sharp and discrete are spread over a band of energy. The spreading up of the energy states is also brought about by the resonance effect between the neighbouring cations, as they are much more closer to each other inside a solid than when in the vapour state. At the ordinary temperature the broadening in some cases increases to such an extent that there is overlapping of the two successive energy states. In such a case the Condon curves for the successive states will either touch or intersect each other. It was pointed out by Mott and Gurney¹⁰ that this is an essential condition for the origin of phosphorescence or fluorescence in solids. In figure 2, let 'a' represent the Pot. E-curve for the ground state, while 'b' and 'b'' represent the

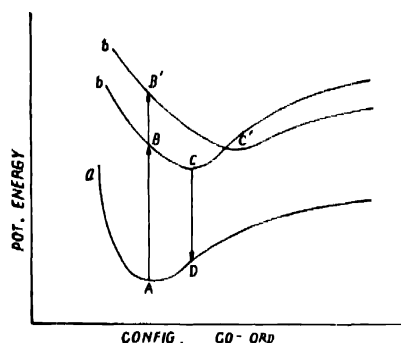


FIGURE 2

a—Ground states

b, b'—Successive excited states.

same for the two successive excited states. If A be the position of the absorbing centre when it absorbs, then, according to the Franck-Condon's principle, it can go to either B or B' by absorbing quanta Ab or Ab' respectively; for there cannot be any change in the relative positions of the atomic nuclei during the absorption of a quantum of radiation. If it goes to B, then, by process of thermal collisions it will part with vibrational energy and come down to the configuration of lowest Pot. E as at C. From C an electronic transition to the ground state is possible by emitting the quantum of radiation represented by CD. This is the simplest case of fluorescence. When it is raised to B' it will come down in an exactly similar manner and reach the point P, where the two successive excited states are supposed to intersect. Thereafter it will either continue its motion along b' and reach C', the point of minimum Pot. E in b' or it may slip down into b through the point of intersection and reach the point C. In the latter case, there will be fluorescence emitting CD as before. In the former, there will be fluores-

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cence if C' is not beyond the curve 'a'; but, if the point C' lies outside the lower curve, no immediate transition is possible and so it will give rise to phosphorescence.

In order to understand the emission spectra due to the Ce^{+++} ions in crystals, we shall suppose that the energy bands due to the three sub-levels of $5D_{3/2}$, which give rise to the three strong absorption bands, overlap each other mutually as shown in figure 3. Now there is the possibility (a) that the energy band due to the lowest of these sub-levels may overlap that due to the state $5D_{5/2}$ or (b) there may be a zone of separation between them.

The overlapping between the energy bands due to the successive excited states is, however, virtual, *i.e.*, it is not to be postulated until the $4f$ -electron is excited to one of these states. So the frequencies of the selective absorption bands due to Ce^{+++} remain unaffected. If the incident radiation corresponds to any one of the absorption bands due to Ce^{+++} ion, the $4f$ -electron will be excited to one or other of the upper states. But the excited electron will part with its energy in thermal collisions and gradually come down as has been pictured above. In case (a) the final level reached by the excited electron in this way will be the $5D_{5/2}$, and then there will be the transition of the electron to the ground term. In Ce^{+++} ion, the ground term is a doublet given by $4^2F_{5/2, 7/2}$. As transitions to either of them is possible from $5D_{5/2}$, two emission bands are to be expected in this case.

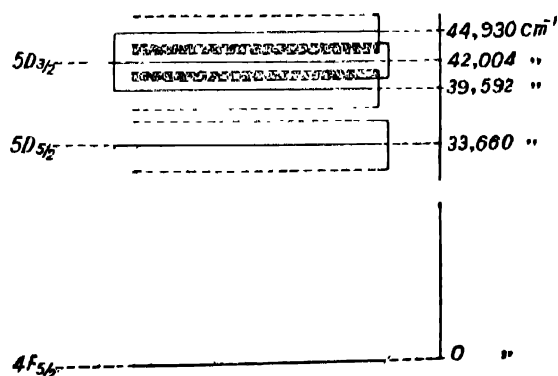


FIGURE 3

In case (b), on the other hand, transition is possible from either of the two states $5D_{3/2}$ and $5D_{5/2}$ to the ground term. This suggests that altogether there will be four emission bands here. But as the transition $5D_{3/2} \rightarrow 4F_{7/2}$ involves a change of two units in 'j', this is much less probable. So that only three strong emission bands are to be anticipated.

The emission spectra observed in the different crystals will be qualitatively explained if it is supposed that in the chloride and sulphate crystals the energy-pattern is as in (a) while in CeF_3 it is as in (b). It has to be shown now if there is any quantitative agreement between the positions of the emission bands observed and those expected from their absorption spectra. For this purpose the energy level diagrams for Ce^{++} ions as revealed by a study of the emission spectra of the different salts are given in figures 4, 5 and 6.

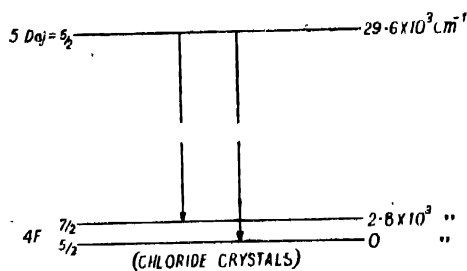


FIGURE 4

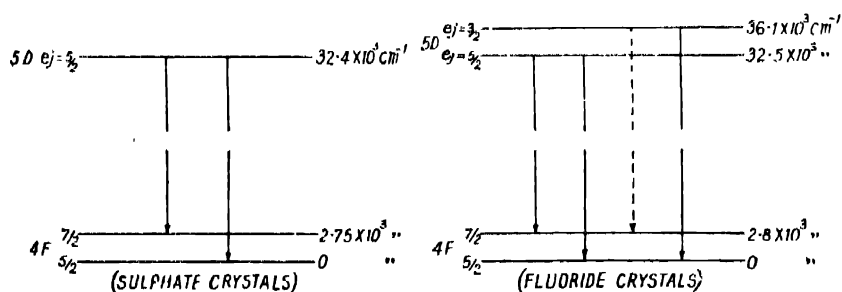


FIGURE 5

FIGURE 6

It is to be noted that in all the three figures the interval between the components of the ground term 4^2F of Ce^{++} is nearly the same, *viz.*, $2,800 \text{ cm}^{-1}$. Also it is in fair agreement with the calculated value $\Delta\nu = 2,500 \text{ cm}^{-1}$ taking the usual value of the screening constant, *viz.*, $\sigma = 34$. As regards the position of the virtual states, it is found from figures 5 and 6 that in the sulphate and fluoride the state $5D_{5/2}$ occupies almost the same position as is found in the case of absorption shown in figure 1. In chloride, the above energy level is slightly depressed. The position of the state $5D_{3/2}$, which is effective only in fluoride, could not be so correlated as the corresponding absorption spectra did not reveal any structure.

ORIGIN OF THE WEAK LUMINESCENCE

The origin of the weak luminescence (observed in CeF_3) on the lower frequency side of the principal bands is not clearly understood. It appeared

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when the exciting frequency was above $40 \times 10^3 \text{ cm.}^{-1}$ and gradually gained in intensity with the increase of the frequency of excitation. As in the sulphate and chloride crystals no such emission was observed even when excited with the high frequencies, it seems that Ce^{++} ions alone are not responsible for its production. That is, the origin of this luminescence is not due to the process 1(a). Let us see if it may be due to the process 1(b) mentioned above. In that case one has to postulate that the ultra-violet radiation is first absorbed by Ce^{++} ions and, when in the metastable state, they transfer their energy to the anions by collisions of the second kind, and the latter give rise to the luminescence. The process is then somewhat analogous to 'sensitized fluorescence' and it requires that the anion must possess excited states below the metastable state in question of the cation. But it is known that in LiF or in CaF_2 the ultra-violet radiation up to a much higher frequency is transmitted undiminished. Since, however, the limit of absorption in CaF_2 (1400Å°), is to the longer wave-length side of (1050Å°) that in LiF , it may be (still more shifted to the longer wave-length side) in CeF_3 , where the polarisation of F^- will be still greater on account of the triply charged cations; further, on account of the presence of defect places in the lattice, absorption may ensue at a still lower frequency.

On this hypothesis, however, one has to explain why such luminescence is absent in the chloride or the sulphate. It is well known that for either of the anions Cl^- and SO_4^{--} , the continuous absorption begins at a lower wave-length than in F^- . And, on account of the continuous absorption by the anions ensuing at much lower frequency, the requisite energy for sensitized fluorescence is not available to the cation. Further, the frequency of the transitions possible in these anions, in case of excitation, may not be within the spectral region investigated and thus may have escaped observation.

In conclusion the writer desires to express his grateful thanks to Prof. D. M. Bose, Ph.D., for his kind interest and helpful suggestions, and to Prof. M. N. Saha, D.Sc., F.R.S., for his kind encouragement during the progress of the work.

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